THE UTILISATION OF HYDROGEN IN UK COAL LIQUEFACTION

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INTRODUCTION

Though at present the North Sea wells provide all the crude oil that the UK requires, this is unlikely to be the case much beyond the end of the decade. As Britain has adequate large coal reserves, the National Coal Board is preparing for this situation by developing two processes to convert coal into liquid hydrocarbons. The main feature of these processes is that they are aimed at the production of premium products such as gasoline, diesel and jet fuels, a feature which could also prove attractive outside the UK.

When producing light hydrocarbons in high yield it is essential to utilise hydrogen efficiently as the production of hydrogen is expensive. In both processes this is achieved by a two-stage conversion. In the first stage the coal is extracted, in the absence of gaseous hydrogen, such that the mineral matter can be removed and the initial coal breakdown products can be stabilised. This makes it possible to use a selective catalyst in the second stage to hydrocrack and refine the coal extract.

The paper describes the two processes under development, and illustrates the utilisation of hydrogen with a set of material balance and hydrogen consumption data for the preparation of gasoline and diesel fuel.

THE PROCESSES

The two processes under development are the Liquid Solvent Extraction (LSE) process and the Supercritical Gas Extraction (SGE) process.

The LSE process involves the use of the high boiling (+ 300°C) fraction from the hydrocracker product to extract coal at about 400°C. Because no gaseous hydrogen is needed at this stage, the extraction is carried out at only a few atmospheres pressure, which is a considerable advantage where solids handling is involved. Sufficient hydrogen transfer to stabilise the extracted material is effected by virtue of the hydrogen donor property of the hydrogenated recycle solvent. High extract yields are obtained as virtually all of the coal except some of the inertinite/fusinite fraction is dissolved. Furthermore by a suitable choice of extraction conditions it is possible to produce a solution that has favourable filtration properties, ie low filtrate viscosity and high filter cake permeability(1).

The clean coal solution (0.04% ash) is reacted with hydrogen over a catalyst at about 425°C and 200 bar, as a result of which the aromatic structures present are hydrogenated and cracked, and oxygen, nitrogen and sulphur are removed. Some of the commercially available petroleum hydrotreating catalysts of the Co/Mo/alumina, Ni/Mo/alumina type are suitable for this duty but other specially formulated catalysts are being investigated.

The hydrocrackate is distilled into three fractions: a naphtha, nominally IPB-200°C, a mid-distillate (200-300°C) and a higher boiling fraction for recycle as coal solvent.

The naphtha is a stable colourless liquid which is rich in naphthenes and contains 13% hydrogen, 400 ppm nitrogen and 10 ppm sulphur. After further vapour phase hydrofining to reduce the nitrogen and sulphur to acceptable levels it can be dehydrogenated by reforming to produce a high octane gasoline. For example, in one test(2) the reformate produced in 95% yield had a RON of 108.

The mid-distillate is nearly colourless and is a mixture of two and three ring hydro-aromatics and naphthenes, and some aromatics. It contains 11% hydrogen, and, like the naphtha, only small quantities of heteroatoms. Batches of mid-distillates have been further hydrotreated to produce diesel fuel for engine tests. Saturation of the aromatic content raised the hydrogen composition to 13% and the overall performance of the fuel in the Ricardo(3) test engine was equivalent to that of current UK road vehicle fuel. It had a Cetane No of 46, and a Bosch Smoke Index that was half that of petroleum gas oil at high load. It had a very low freezing (-78°C) and low cold filter plugging point (-50°C) which indicated a complete absence of hydrocarbon waxes.

The naphtha, mid-distillate and hydrogenated mid-distillates have also been assessed as steam cracker feedstocks for the production of olefins and aromatics(2). Tests made by ICI gave good cracking patterns: 33% olefins and 24% aromatics, and ICI gave the hydrogenated mid-distillate a commercial value index of 95 compared with 100 for a standard petroleum naphtha.

In an integrated process as shown in Fig 1, coal is the only input and extra coal will be required to supplement the extraction residues to provide the hydrogen and process energy. Preliminary estimates from a study of a commercial scale plant have indicated an overall thermal efficiency of 65-70%.

The process has been developed at the Coal Research Establishment on a 2 kg/h scale. An integrated plant (Fig 2) has been run for long continuous periods, up to 1200 h, providing distillates for assessment and data for the design of larger plants. The design of a 1 tph plant has already been prepared and it is hoped to build it within the next two years. It should then be possible to go straight to a single stream plant consuming 2-5000 tpd and so to full scale commercial production by the mid-1990s.

The Supercritical Gas Extraction process (Fig 3) involves the use of an aromatic solvent close to its critical temperature to dissolve coal at about 420°C. In this condition the fluid is less dense and less viscous than a liquid would be, but the molecules are sufficiently close together to act as a solvent. At ambient conditions the solvent is a liquid so can be used to slurry the coal. The supercritical solvent selectively extracts the smaller molecular species which contain more hydrogen than the rest of the coal(4). The carbonaceous residue recovered after extraction is suitable for gasification and combustion to provide the process requirements as shown in the Figure. For high volatile bituminous coals, an extract yield sufficient to provide this overall balance, between 40% and 50% of the daf coal, can be obtained. This is also the case for lower rank coals, depending on their composition.

No hydrogen gas is needed in the extraction stage, but the nature of the solvent leads to an extraction pressure of 200 bar. Depressurisation of the supercritical solution stream causes the extract to be precipitated and allows the solvent to be recycled. The extract is hydrocracked, together with recycled heavy oil, to produce similar products to those obtained in the LSE process at an estimated overall thermal efficiency of 65%.

The SGE method of extraction has been demonstrated on a 5 kgh^{-1} scale, and will be studied at a scale of 1 tph as part of the test facility, already referred to in the LSE process description.

HYDROGEN UTILISATION

In order to illustrate the utilisation of hydrogen in NCB coal liquefaction one set of data for the LSE process has been considered in detail. The data were obtained from the integrated unit shown in Fig 2, when equilibrium conditions were assumed to prevail.

A UK bituminous coal - Annesley - was used and its composition is shown in Table 1. The yields of products and hydrogen consumption are given in Table 2. The liquid products, under the specified set of conditions, consisted of naphtha and mid-distillate and a considerable yield of pitch. The filter cake liquids shown were not recovered in the test but an estimate has been made in Table 2 of the effect of recovering these liquids by washing and passing them to the hydrocracker with the bulk of the extract solution.

The utilisation of hydrogen in the test is shown by the hydrogen account of Table 3. This shows that 66% of the hydrogen in the feedstock appears in the liquid products and is a quantitive measure of the efficiency of hydrogen utilisation during liquefaction.

As the naphtha and mid-distillate products are considerably refined during hydrocracking, their conversion to gasoline and diesel fuel requires little further hydrogen consumption. The final yield values are given in Table 4. The low gas yield in the overall process contributes significantly to the efficient utilisation of hydrogen and the relatively high thermal efficiency of the process.

The pitch obtained in the run studied can be reduced and possibly eliminated by employing more severe hydrocracking conditions. However, the pitch is a useful product as it could be used as an electrode binder, a source of carbon black or alternatively it could be coked to produce electrode carbon. Some coking tests have been made and the following yields obtained: coke 51%; distillates 39%; gas 10%. The liquid recovered in the latter case would supplement the solvent inventory of the process and would allow some of the lighter solvent to be removed as products.

Alternative options of this kind have been examined in a study of the commercial scale operation of the process carried out in conjunction with an International Chemical Engineering Contractor. The results from these studies showed that neither the plant cost nor the overall thermal efficiency varied greatly between the options.

The above data relate to the processing of bituminous coal. Lignites and brown coals can also be extracted by this process with the additional advantage that much of the high oxygen content in these coals is eliminated in the extraction stage as CO_x thus in principle saving hydrogen. It appears that when hydrogen gas is used during the extraction stage oxygen is removed as water. However although tests with brown coals and lignites have been made in laboratory experiments, no equilibrium processing data are as yet available.

CONCLUSIONS

The two liquefaction processes being developed by the National Coal Board offer the prospect of an efficient production of transport fuels from coal.

Test results from small pilot plant indicate yields, based on daf coal to liquefaction, of 14% gasoline and 35% diesel fuel, both meeting the current UK road fuel specifications. The hydrogen consumption in this test work was 6.7% daf coal and the hydrogen recovered in the liquid products was equivalent to 66% of the hydrogen fed to the process.

These yields do not represent the maximum values as an additional 21% high boiling liquid product was available for further conversion and alternative processing schemes for the conversion of this material are under investigation.

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Table 1

Analysis of Annesley Coal

International Classification 633

Carbon	84.8% daf coal
Hydrogen	5.5% " "
Oxygen	7.5% " "
Nitrogen	1.9% " "
Sulphur	0.8% as received
Volatile matter	38.6% daf coal
Vitrinite	77%
Exinite	4%
Inertinite) Fusinite)	19%
Swelling number	6½

Table 2

Product Yields and Hydrogen Consumption in LSE Process Unit

Material	Weight without cake washing	Weight with cake washing
Input		
Coal (daf basis)*	100	100
Hydrogen consumed	5.7	6.0
Products		
C_1-C_3 gases	10	10
C_4-170°C naphtha	13	13
170-350°C mid-distillate	29	35
$>$ 420°C pitch	15	21
Cake liquids	17	4
Undissolved coal	12	12
CO_x, H_2O, H_2S, NH_3	10	11

*This does not include the additional coal (approximately 60 parts by weight) needed to supplement the filter cake for process heat, power and hydrogen production.

Table 3

The Hydrogen Account for LSE Test Run

Conversion of 100 units daf coal

Hydrogen In			Hydrogen Out		
Coal (daf basis)	=	5.5	Filter cake	=	0.8
			Hydrocarbon gases	=	2.2
Hydrogen consummed	=	6.0	Heterogases	=	1.1
			Naphtha	=	1.8
			Mid-distillate	=	4.0
			Pitch	=	1.6
TOTAL	=	11.5	TOTAL	=	11.5

$$\text{Hydrogen Retrieval} = \frac{\text{Hydrogen in Liquid Products}}{\text{Hydrogen in Coal + Added Hydrogen}} \times 100 = 66\%$$

Table 4

Products and Hydrogen Consumption after Secondary Refining

Material	Weight without cake washing	Weight with cake washing
Input		
Coal (daf basis)*	100	100
Hydrogen consumed	6.2	6.7
Products		
C_1-C_3 gases	10	11
Gasoline	13	14
Diesel fuel	29	35
Pitch	15	21

*This does not include coal needed for process heat, power and hydrogen production.

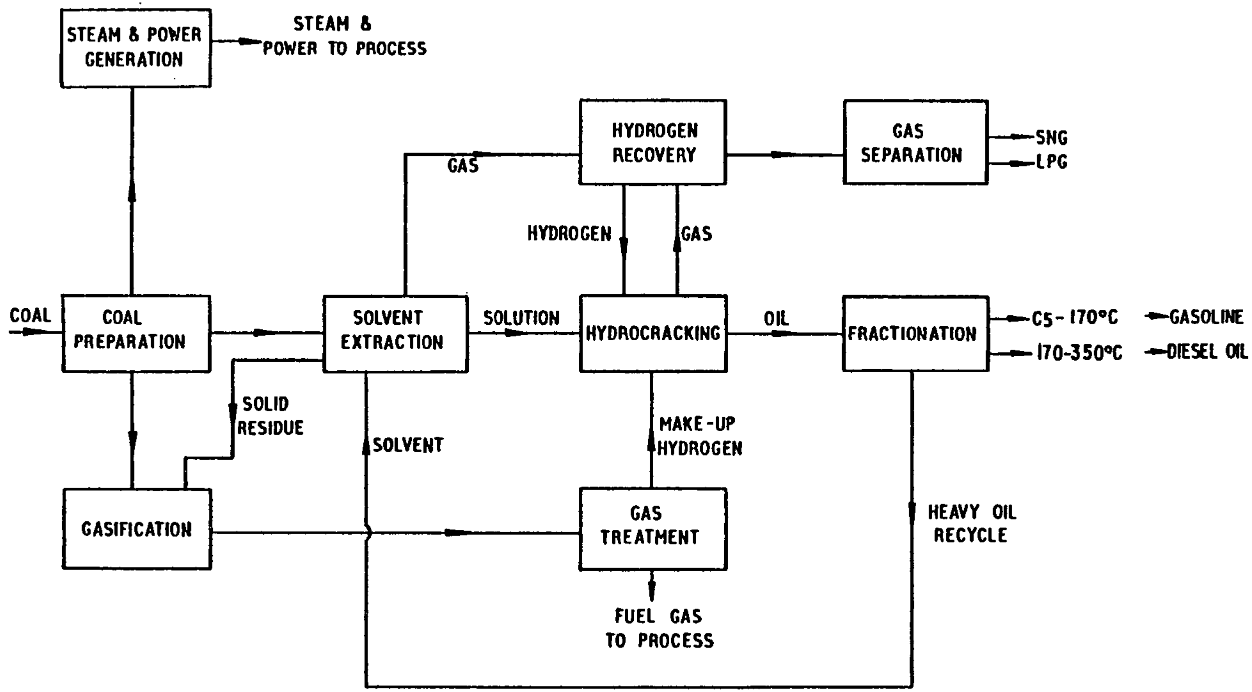

FIG. I NCB LIQUID SOLVENT EXTRACTION PROCESS

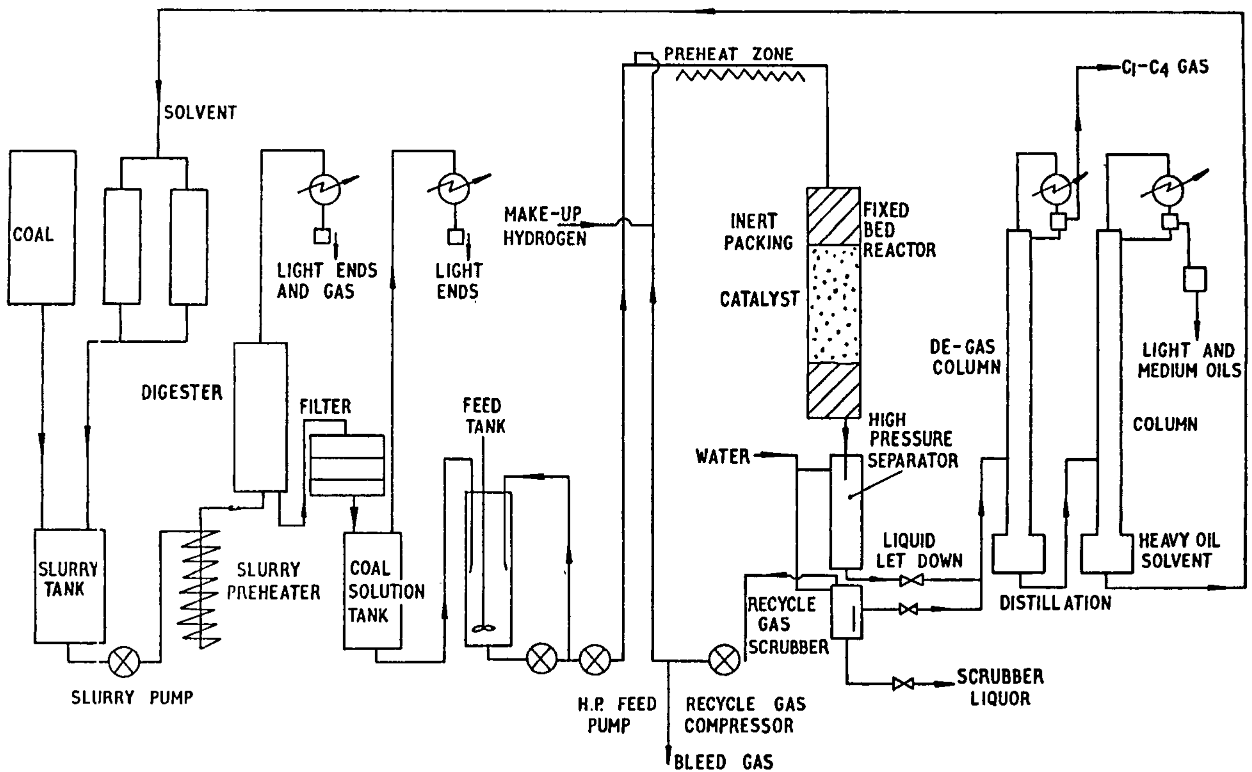

FIGURE 2. INTEGRATED SOLVENT EXTRACTION / CONTINUOUS HYDROCRACKING UNIT

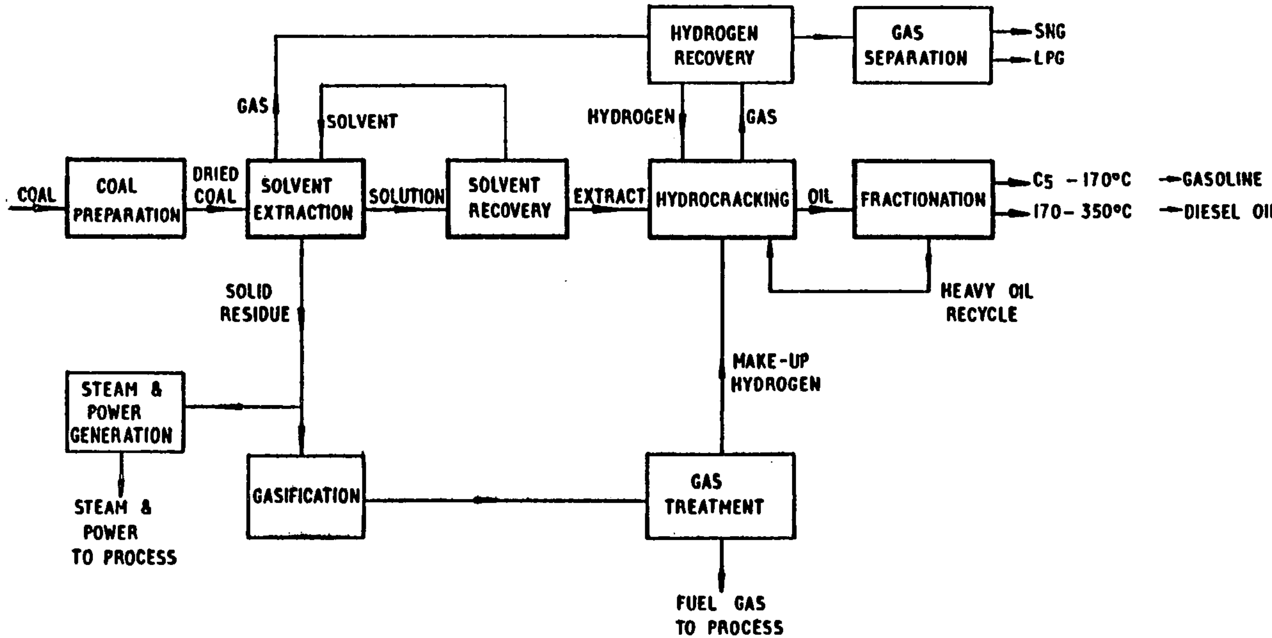

FIG. 3 NCB SUPERCRITICAL GAS EXTRACTION PROCESS